

# DAMPING OF DROP OSCILLATIONS BY SURFACTANTS AND SURFACE VISCOSITY

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## Abstract

The roles played by surfactants and interfacial rheology on damping the shape oscillations of liquid drops are analyzed for the case of axisymmetric shape oscillations of a nearly spherical liquid drop surrounded by another fluid in the absence of gravity. Both fluids are taken to be viscous, although the Reynolds number associated with the shape oscillations is assumed large enough that deviations from inviscid flow are only present in thin Stokes boundary layers near the no-slip interface. Also, an insoluble surfactant is assumed to be present at the interface and surface tension is taken to be a linearly decreasing function of local surfactant concentration. This surfactant layer is further assumed to behave as a two-dimensional Newtonian fluid layer characterized by surface shear and dilatational viscosities.

Under these conditions, several sources can be identified for mechanical dissipation and the ultimate damping of the shape oscillations of the drop. These include viscous effects associated with the bulk fluids that appear in two distinct forms: one associated with the oscillatory viscous boundary layers which form near the interface between the drop and surrounding fluid, and the other associated with the flows far from the interface which resemble potential flow although they dissipate energy through weak viscous action. Surfactants and surface rheology additionally contribute to dissipation in other ways. The surface shear and dilatational viscosities dissipate energy within the interface in much the same way as the viscous dissipation in the three-dimensional bulk fluids just mentioned. Moreover, as various parts of the interface locally increase or decrease in area during shape oscillations, the concentration of surfactants locally decreases or increases. This leads to gradients in surfactant concentration on the interface where the process of gradient diffusion of surfactants within the interface, itself an irreversible process, leads to energy dissipation. Also, the Marangoni flow resulting from this non-uniformity in surface tension contributes to viscous damping.

This paper outlines the derivation of a general mechanical energy equation for such a system. It contains dissipation terms accounting for each of the mechanisms described above. The energy equation is applied to a slightly perturbed axisymmetric drop oscillating in a low-density surrounding fluid to derive an approxi-

mate ordinary differential equation (resembling that of a damped harmonic oscillator) which describes the time evolution of pure shape modes.

In parallel to the analytical treatment, the implementation of a boundary integral method for potential (i.e. inviscid) flow is presented for the case of a two-dimensional drop oscillating in vacuum. The effect of a constant surface dilatational viscosity is included in the computations by combining the tangential and normal components of the dynamic boundary condition into a single equivalent expression. This expression, combined with Bernoulli's equation for the pressure, the kinematic boundary condition and the regularized Fredholm integral equation of the second kind representing Laplace's equation for potential flow, produces a coupled set of nonlinear equations that allow the time evolution of the drop's shape to be followed. Surface dilatational viscosity is shown to have a damping effect on the free oscillations of the drop.

## 1 Introduction

Shape oscillations of drops and bubbles have been studied since the works of Kelvin [6] and Rayleigh [15] who determined the linearized frequencies of inviscid shape modes. Their work was extended by Lamb [7], Reid [16] and Valentine *et al.* [19], who included estimates of damping by weak viscous effects in the bulk. Miller & Scriven [11] and Marston [10] further identified the important role played by the boundary layers near the interface in damping the oscillations. The additional effects of surfactants and surface rheology, known to have a strong influence on the base frequency and damping rates of drops [1] and bubbles [3], have been analyzed by Lu & Apfel [8] and Tian *et al.* [18]. Numerical studies, based upon the boundary integral method, of the dynamics of weakly viscous drops were initiated by Lundgren and Mansour [9] and have been extended to include surfactant effects by Tian *et al.* and Apfel *et al.* [1] used numerical simulations in conjunction with experimental studies of drops in microgravity to quantify the important role of surfactants in such systems.

The present contribution also focuses on the role of surfactants and surface rheology on drop oscillations in the absence of gravity. In addition to Marangoni effects which arise due to non-uniformity of surface tension

## 2 THE ENERGY EQUATION

along the interface in the presence of surfactants, the interfacial layer of adsorbed surfactants may also possess separate rheological properties [4] which change the dynamics. Our goal is to identify the specific mechanisms through which surfactants and surface rheology affect the system and quantify each of them. An approach based on a global mechanical energy balance is outlined and allows the damping rates of pure shape modes by bulk viscosity, surface viscosity, boundary layer dissipation, and surfactant transport to be quantified. This energy equation generalizes the work of Hsu & Apfel [5], who used a simplified energy equation to approximate the rate of damping of a viscous drop with a constant surface tension oscillating in the quadrupole mode. Supplementing the analytical treatment, a numerical implementation of the boundary integral method for potential flow is described which incorporates the effects of surface viscosity. The method is presented for the oscillations of two-dimensional liquid drops possessing a constant surface dilatational viscosity.

### 2 The Energy Equation

Consider a liquid drop of density  $\hat{\rho}$  and viscosity  $\hat{\mu}$  to be suspended in an infinite medium of density  $\rho$  and viscosity  $\mu$ , in the absence of gravity. If both fluids are assumed to be incompressible and Newtonian, the continuity and momentum equations take the forms:

$$\nabla \cdot \mathbf{v} = 0, \quad \rho \frac{D\mathbf{v}}{Dt} = \nabla \cdot \mathbf{\Pi} \quad \text{for } \mathbf{x} \in V(t), \quad (1)$$

$$\nabla \cdot \hat{\mathbf{v}} = 0, \quad \hat{\rho} \frac{D\hat{\mathbf{v}}}{Dt} = \nabla \cdot \hat{\mathbf{\Pi}} \quad \text{for } \mathbf{x} \in \hat{V}(t), \quad (2)$$

where  $\mathbf{v}$  and  $\hat{\mathbf{v}}$  respectively refer to the medium and drop velocity fields,  $V(t)$  and  $\hat{V}(t)$  are the material volumes of the medium and drop, and the stress tensors  $\mathbf{\Pi}$  and  $\hat{\mathbf{\Pi}}$  are given by

$$\mathbf{\Pi} = -p\mathbf{I} + 2\mu\mathbf{E}, \quad \mathbf{E} = \frac{1}{2}[(\nabla\mathbf{v}) + (\nabla\mathbf{v})^T], \quad (3)$$

$$\hat{\mathbf{\Pi}} = -\hat{p}\hat{\mathbf{I}} + 2\hat{\mu}\hat{\mathbf{E}}, \quad \hat{\mathbf{E}} = \frac{1}{2}[(\nabla\hat{\mathbf{v}}) + (\nabla\hat{\mathbf{v}})^T]. \quad (4)$$

Here  $p$  and  $\hat{p}$  represent the pressures in the two fluids,  $\mathbf{I}$  is the isotropic unit tensor, and  $\mathbf{E}$  and  $\hat{\mathbf{E}}$  are the symmetric and traceless rate-of-strain tensors.

These field equations need to be supplemented by boundary conditions at infinity – that the velocity field vanishes and the pressure tends to a constant value – and at the interface  $S(t)$  between the drop and medium. The interface is assumed to be covered with surfactants

and therefore possesses its own rheological properties, which may be characterized by the surface stress tensor  $\mathbf{\Pi}_s$  [4]. The boundary conditions at the interface thus assume the respective forms [4]:

$$\left. \begin{aligned} \mathbf{v} = \hat{\mathbf{v}} &\equiv \mathbf{v}^s \\ \hat{\mathbf{n}} \cdot (\mathbf{\Pi} - \hat{\mathbf{\Pi}}) &= -\nabla_s \cdot \mathbf{\Pi}_s \end{aligned} \right\} \quad \text{for } \mathbf{x} \in S(t). \quad (5)$$

The velocity at the interface is denoted by  $\mathbf{v}^s$  and is equal to the fluid velocities in the medium and drop evaluated at  $S$ . The surface stress tensor is also assumed to be “Newtonian” and defined by a Boussinesq-Scriven constitutive relationship of the form [4, 12, 17]

$$\mathbf{\Pi}_s = \sigma\mathbf{I}_s + 2\mu_s\mathbf{E}_s + \kappa_s\mathbf{I}_s(\nabla_s \cdot \mathbf{v}^s). \quad (6)$$

In this expression,  $\sigma$ ,  $\mu_s$ , and  $\kappa_s$  respectively refer to interfacial tension, surface shear viscosity, and surface dilatational viscosity. Also,  $\mathbf{I}_s = \mathbf{I} - \hat{\mathbf{n}}\hat{\mathbf{n}}$  is the surface unit tensor,  $\nabla_s = \mathbf{I}_s \cdot \nabla$  is the surface gradient, and  $\mathbf{E}_s$  is the symmetric and traceless surface rate-of-strain tensor defined by

$$\mathbf{E}_s = \frac{1}{2}[(\nabla_s \mathbf{v}^s) \cdot \mathbf{I}_s + \mathbf{I}_s \cdot (\nabla_s \mathbf{v}^s)^T] - \frac{1}{2}\mathbf{I}_s(\nabla_s \cdot \mathbf{v}^s). \quad (7)$$

The derivation of the mechanical energy equation begins by dot multiplying the momentum equation in (1) by  $\mathbf{v}$ , the momentum equation in (2) by  $\hat{\mathbf{v}}$ , integrating over the respective material volumes  $V(t)$  and  $\hat{V}(t)$ , and adding the resulting equations. Assuming that the concentration of surfactants  $\Gamma$  varies only slightly from the equilibrium concentration  $\Gamma_o$ , the surface tension may be modeled as a linearly decreasing function of the form

$$\sigma(\Gamma) = \sigma_o + \beta(\Gamma - \Gamma_o), \quad \beta = \frac{d\sigma}{d\Gamma}(\Gamma_o) < 0. \quad (8)$$

With the aid of the boundary conditions (5), as well as the bulk and surface Reynolds Transport Theorems and Divergence Theorems [2, 12], the following energy equation is finally obtained [13]

$$\begin{aligned} \frac{d}{dt} \{K.E. + S.E.\} = & \\ & - \int_{V(t)} 2\mu(\mathbf{E} : \mathbf{E}) dV - \int_{\hat{V}(t)} 2\hat{\mu}(\hat{\mathbf{E}} : \hat{\mathbf{E}}) d\hat{V} \\ & - \int_{S(t)} [2\mu_s(\mathbf{E}_s : \mathbf{E}_s) + \kappa_s(\nabla_s \cdot \mathbf{v}^s)^2] dS \\ & - \int_{S(t)} \beta(\Gamma - \Gamma_o)(\nabla_s \cdot \mathbf{v}^s) dS, \end{aligned} \quad (9)$$

where

$$\begin{aligned}
 K.E. + S.E. = & \\
 & \int_{V(t)} \frac{1}{2} \rho v^2 dV + \int_{V(t)} \frac{1}{2} \hat{\rho} \hat{v}^2 dV \\
 & + \int_{S(t)} \sigma_o dS
 \end{aligned} \quad (10)$$

is the total kinetic energy plus surface potential energy of the system. The first two terms on the right-hand side of (9) represent dissipation in the two bulk fluids. The next two terms are similarly identified as dissipation terms arising from surface shear and dilatational viscosities. The last term on the right-hand side of (9) requires further attention. This term can be shown [13] to be either dissipative or provide an additional surface energy storage depending on the surface Peclet number characterizing surfactant transport. The complete surfactant transport equation for an insoluble surfactant is itself given by

$$\frac{\partial \Gamma}{\partial t} + \mathbf{v}^s \cdot \nabla_s \Gamma + (\nabla_s \cdot \mathbf{v}^s) \Gamma = \nabla_s \cdot (D_s \nabla_s \Gamma), \quad (11)$$

where  $D_s$  is the surface diffusivity of surfactants.

The mechanical energy equation obtained above may be used to derive an approximate ordinary differential equation (ODE) which describes the evolution of pure shape modes of three-dimensional axisymmetric liquid drops [13]. The key results are outlined here and the reader is referred to the original article [13] for details. The approximation involves using the potential flow solution to estimate the kinetic energy and the dissipation integrals in the bulk, the oscillatory Stokes boundary layer velocity field to estimate the dissipation rate in the thin layers surrounding the interface, and the surface velocity from this analysis to estimate the surface dissipation integrals. For the quadrupole mode of oscillation, with the radial coordinate of surface points given by

$$r = a_o [1 + f(t) P_2(\cos \theta)], \quad (12)$$

and the surfactant concentration by

$$\Gamma(\theta, t) = \Gamma_o + g(t) P_2(\cos \theta), \quad (13)$$

where  $a_o$  and  $\Gamma_o$  are the respective equilibrium radius and surfactant concentration,  $f(t)$  and  $g(t)$  the time-dependent amplitudes of deformation and concentration change (both assumed small),  $P_2$  the second Legendre polynomial, and  $\theta$  the polar angle measured from the axis of symmetry, the following system of ODEs may

be obtained to describe the time-dependent dynamics:

$$\begin{aligned}
 \frac{\hat{\rho} a_o^3}{2} \ddot{f} + 4\sigma_o f &= -\beta g \\
 &- \left[ 5\hat{\mu} a_o + 12\mu_s + \kappa_s + \frac{25a_o^2}{12\sqrt{2}} \sqrt{\omega_{2,o} \mu \rho} \right] \dot{f}, \\
 \dot{g}(t) + \frac{6D_s}{a_o^2} g(t) &= \Gamma_o \dot{f}(t).
 \end{aligned}$$

Here,  $\omega_{2,o}$  is the base frequency of the quadrupole shape mode given by  $(8\sigma_o/\hat{\rho}a_o^3)^{1/2}$ . The coefficient of  $\dot{f}$  on the right-hand side of the first equation represents damping due to viscous dissipation in the bulk liquid inside the drop, due to surface shear and dilatational viscosities, and due to the Stokes boundary layer in the gas surrounding the drop. In addition, the term which couples that equation to surfactant concentration  $g(t)$  can be partially dissipative, depending on the value of the surface Peclet number  $\omega_{2,o} a_o^2 / D_s$  [13]. These results are obtained in the limit where the density and viscosity of the drop phase are large compared with those of the surrounding fluid.

### 3 Boundary Integral Method

The numerical problem considers the shape oscillations of a *two*-dimensional inviscid drop in vacuum without gravity. It is assumed that the drop has an undeformed equilibrium radius  $a_o$  and the interface is highly contaminated with insoluble surfactants so that the interfacial properties  $\sigma_o$ ,  $\mu_s$ , and  $\kappa_s$  are constants. Parameterizing all the variables with arclength  $s$ , using the inviscid stress tensors  $\hat{\Pi} = -p\mathbf{I}$  and  $\Pi = 0$ , and expressing the gradient  $\nabla = \hat{s}\partial/\partial s + \hat{n}\partial/\partial n$  and velocity of the interface  $\mathbf{v}^s = \hat{s}v_s + \hat{n}v_n$  in terms of local coordinates  $\hat{s}$  and  $\hat{n}$ , the tangential and normal components of the dynamic boundary condition in (5) take the respective forms:

$$0 = \frac{\partial}{\partial s} \left[ \frac{\partial v_s}{\partial s} + v_n \mathcal{C} \right], \quad (14)$$

$$p = \mathcal{C} \left\{ \sigma_o + \kappa_s \left[ \frac{\partial v_s}{\partial s} + v_n \mathcal{C} \right] \right\}, \quad (15)$$

where  $\mathcal{C}$  is the local curvature of the two-dimensional interface. By first noting that  $v_s$  is necessarily periodic in total arclength  $L$  and integrating (14) twice with respect to arclength around the drop these two components may be combined to obtain

$$p = \mathcal{C} \{ \sigma_o + \kappa_s B(t) \}, \quad (16)$$

## 4 CONCLUSIONS

where the time-dependent quantity  $B(t)$  is defined by

$$B(t) = \frac{1}{L} \int_0^L v_n C ds. \quad (17)$$

Nondimensionalizing time with  $(\rho R^3/\sigma_o)^{1/2}$ , length with  $a_o$ , and mass with  $\rho a_o^3$  the boundary integral formulation of the governing equations for this system at a particular instant in time are

$$\int_0^L K_1(s_i, s)[q(s) - q(s_i)] ds = \phi(s_i), \quad (18)$$

$$\psi(s_i) = - \int_0^L K_2(s_i, s)[q(s) - q(s_i)] ds \hat{\mathbf{k}}, \quad (19)$$

$$\frac{D\phi}{Dt}(s) = \frac{1}{2} |\mathbf{v}^s(s)|^2 - C(s)\{1 + \kappa_s^* B\}, \quad (20)$$

$$\frac{d\mathbf{x}}{dt}(s) = \mathbf{v}^s(s). \quad (21)$$

Equation (18) represents the regularized double-layer potential boundary integral formulation of Laplace's equation for potential flow [14].  $K_1$  is the weakly singular kernel defined as the projection of the gradient of the two-dimensional Green's function for Laplace's equation in the direction normal to the interface,  $q(s)$  is a distribution of dipole densities around the drop interface, and  $\phi$  is the scalar velocity potential.  $\psi = \psi \hat{\mathbf{k}}$  is the vector velocity potential perpendicular to the plane and is related to the velocity of the surface through its curl,  $\nabla \times \psi = \mathbf{v}^s$ . This vector velocity potential also relates to the distribution of dipole densities through an integral containing the weakly singular kernel  $K_2$ , which is defined as the cross product of the unit normal with the gradient of the two-dimensional Green's function.

The dynamic boundary condition (16) has been used with Bernoulli's unsteady equation for pressure to obtain (20), where the time derivative is with respect to an observer moving with the velocity of the interface  $\mathbf{v}^s$  and  $\kappa_s^* = \kappa_s(\sigma_o/\rho R^3)^{1/2}$  is the nondimensional surface dilatational viscosity. Equation (21) represents the kinematic boundary condition.

The above equations were discretized by dividing the periodic boundary into  $N$  equally-spaced nodes in the interval  $0 < s < L$ . All derivatives were calculated using standard  $\mathcal{O}[(\Delta s)^6]$  finite-difference schemes and the regularized integral relations in (18) and (19) were discretized into matrix relations using a trapezoidal quadrature rule between the nodes. The numerical scheme first initialized the shape of the drop  $\mathbf{x}$  and the scalar velocity potential  $\phi$ . The velocity of the interface was then calculated using LU decomposition to solve the matrix

equivalent of (18), performing the matrix multiplication in (19), and taking derivatives of the vector velocity potential with respect to arclength. Using the updated velocity of the interface and curvature, the scalar velocity potential and drop shape could be integrated in time using a fourth-order Runge-Kutta scheme. To prevent clustering and allow for the calculation of the derivatives, the nodes were redistributed to equal spacing in arclength after each time-step. The accuracy of the numerical method was checked by calculating the conserved quantities of total energy and volume in time. Interestingly, the numerical problems reported by [9], arising from the instability of modes with wavelength twice the nodal spacing, did not appear in these two-dimensional calculations.

Figure 1 shows an example of the damping effects of surface dilatational viscosity for an initially perturbed two-dimensional inviscid drop. The calculation used 40 nodes to simulate nearly 40 oscillation periods in the quadrupole mode of moderate initial amplitude. Alternate plots of similar energy versus time curves reveal that the attenuation in time due to surface dilatational viscosity in two-dimensional drops cannot be represented by an exponential or power law.

## 4 Conclusions

An energy equation has been derived for the general case of a viscous drop suspended in a viscous medium with surfactants contaminating the interface. It contains terms clearly identifying dissipation contributions from the viscous effects in the bulk fluids, surface shear and dilatational viscosity effects in the interface, and surfactant transport.

An efficient numerical boundary integral method has been developed which incorporates the effects of a constant surface dilatational viscosity in simulations of an oscillating two-dimensional inviscid drop. Surface dilatational viscosity is shown to have a significant damping effect on the otherwise undamped inviscid oscillations. This damping was found to be neither an exponential nor a power law.

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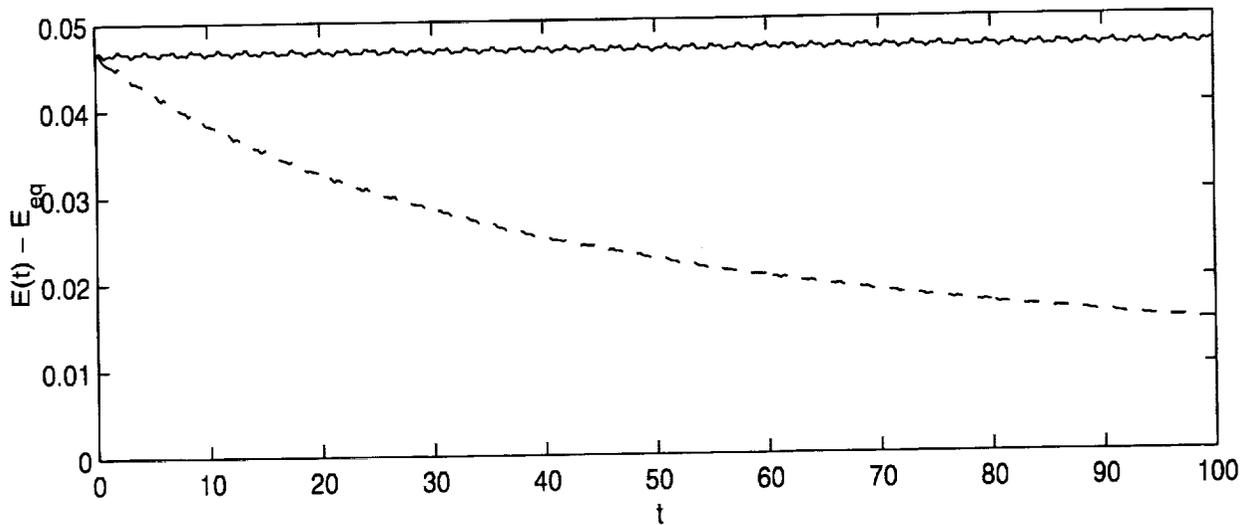


Figure 1: Total energy of the drop versus time after an initial condition  $r = 1 + 0.1 \cos(2\theta)$  and  $\phi = 0$  for the cases  $\kappa_s^* = 0$  (solid line), and  $\kappa_s^* = 1$  (dashed).

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